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Significant progress has been made toward the ultimate goal of a comprehensive framework for systematic analysis of highly excited vibrational states of molecules. Traditional methods are predicated on assignment of eigenstates in terms of quantum numbers, such as the number of quanta in each normal mode, which are physically meaningful only in the low-energy, near-harmonic regime. What is needed is a new or at least much more general framework for spectra complicated by strong interactions among some or all of the degrees of freedom. We have been working toward such a framework through a systematic quest for understanding of the complex semiclassical dynamics underlying the quantum spectrum of the molecule. The main accomplishments achieved under this contract include: (1) determination of spectral patterns associated with phase space bifurcation structure and related spectral assignments with new quantum numbers; (2) assignment of spectra of polyatomics with three or more coupled degrees of freedom, following a bifurcation analysis of a chaotic Hamiltonian obtained from spectroscopic quantum fitting Hamiltonians; (3) the discovery of precessional modes in the bending spectra of acetylene, with assignment and related spectral patterns, following a bifurcation analysis of the spectral fitting Hamiltonian.		
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**FINAL TECHNICAL REPORT.
DYNAMICS AND SPECTRA OF HIGHLY EXCITED
MOLECULES F49620-92-J-0035.**

March 28, 1995

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SENIOR RESEARCH PERSONNEL: Dr. Zimin Lu, Dr. John Rose

JUNIOR RESEARCH PERSONNEL: Mr. Gengxin Chen, Mr. John Svitak, Mr. Shuangbo Yang

PUBLICATIONS:

PUBLICATIONS SUPPORTED UNDER PRIOR AFOSR SPONSORSHIP: 11/1/87 - 10/31/90.

1. M.E. Kellman and E.D. Lynch, reply to "Comment on Semiclassical Phase Space Evolution of Fermi Spectra", J. Chem. Phys. 89, 3396 (1988).
2. L. Xiao and M.E. Kellman, "Unified Semiclassical Dynamics for Molecular Resonance Spectra", J. Chem. Phys. 90, 6086 (1989).
3. M.E. Kellman and L. Xiao, "New Assignment of Vibrational Spectra of Molecules with the Normal-to-Local Modes Transition", Chem. Phys. Lett. 162, 486 (1989).
4. Z. Li, L. Xiao, and M.E. Kellman, "Phase Space Bifurcation Structure and the Generalized Local-to-Normal Transition in Resonantly Coupled Vibrations", J. Chem. Phys. 92, 2251 (1990).
5. J.M. Standard, E.D. Lynch, and M.E. Kellman, "Bootstrap Approach to Fitting Spectra of Molecules with Classically Chaotic Dynamics", J. Chem. Phys. 93, 159 (1990).
6. C. Jaffe and M.E. Kellman, "Localized Chaos and Partial Assignability of Dynamical Constants of Motion in the Transition to Molecular Chaos", J. Chem. Phys. 92, 7196 (1990).
7. L. Xiao and M.E. Kellman, "Catastrophe Map Classification of the Generalized Normal-Local Transition in Fermi Resonance Spectra", J. Chem. Phys. 93, 5805 (1990).

8. M.E. Kellman, "Approximate Constants of Motion for Vibrational Spectra of Many-Oscillator Systems with Multiple Anharmonic Resonances", *J. Chem. Phys.* 93, 6630 (1990).
9. M.E. Kellman and L. Xiao, "New Assignment of Fermi Resonance Spectra", *J. Chem. Phys.* 93, 5821 (1990).

PUBLICATIONS SUPPORTED UNDER AFOSR SPONSORSHIP IN CURRENT GRANT PERIOD: 11/1/91 - PRESENT.

10. J.M. Standard and M.E. Kellman, "Potential Energy Surfaces from Highly Excited Spectra Using the Bootstrap Fitting Method: Two-Dimensional Surfaces for Water and Ozone", *J. Chem. Phys.* 94, 4714 (1991).
11. M.E. Kellman, Z. Li, and L. Xiao, "Bond Selected Bimolecular Reactivity and Phase Space Structure of Intramolecular Excited States", *Chem. Phys. Lett.* 181, 141, (1991).
12. M.E. Kellman, Z. Li, and L. Xiao, "Bond Selected Bimolecular Reactivity and Phase Space Structure of Intramolecular Excited States", *Chem. Phys. Lett.* 181, 141, (1991).
13. M.E. Kellman and G. Chen, "Approximate Constants of Motion and Energy Transfer Pathways in Highly Excited Acetylene", *J. Chem. Phys.* 95, 8671 (1992).
14. "Spectral Patterns and Dynamical Bifurcation Analysis of Highly Excited Molecular Vibrations", J. Svitak, Z. Li, J. Rose, and M.E. Kellman, *J. Chem. Phys.* 102, 4340 (1995).

In Press:

15. Michael E. Kellman, "Dynamical Analysis of Highly Excited Vibrational Spectra: Progress and Prospects", refereed chapter in press in "Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping", H.-L. Dai and R.W. Field, eds.
16. "Algebraic Methods in Spectroscopy", invited article, submitted to *Annual Reviews of Physical Chemistry*, 1995.

Manuscripts in Preparation:

17. "Precessional Modes in Coupled Torsional Spectra of Benzophenone: Dynamical Bifurcation Analysis", John Rose, Z. Li, L. Xiao, J. Svitak, and M.E. Kellman, in preparation.
18. "Precessional Modes in Coupled Bending Modes of Acetylene: Dynamical Bifurcation Analysis", J. Rose, J. Svitak, and M.E. Kellman, in preparation.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This report summarizes work on theoretical analysis of highly excited vibrational spectra of small molecules, continuing research conducted under AFOSR sponsorship under Contract F49620-92-J-0035. Significant strides have been made toward the ultimate goal of a comprehensive framework for systematic analysis of highly excited vibrational states of molecules. The basic motivation arises from the view that the traditional spectroscopic picture of states defined in terms of normal mode quantum number assignments is fundamentally

inadequate for the highly excited, strongly coupled, anharmonic regime. All the work described here takes the general outlook that the road to progress lies in harnessing recent developments in nonlinear dynamical systems to problems of highly excited states. Detailed high-energy spectra of states with many quanta spread throughout the vibrational and rotation-vibration degrees of freedom present unprecedented challenges for spectral interpretation and organization of data into intelligible patterns. Traditional methods are predicated on assignment of eigenstates in terms of quantum numbers, such as the number of quanta in each normal mode, which are physically meaningful only in the low-energy, near-harmonic regime. In highly excited spectra, these zero-order quantum numbers are destroyed by the strongly coupled dynamics, which means the spectra become unassignable in ordinary terms. What is needed is a new or at least much more general framework for spectra complicated by strong interactions among some or all of the degrees of freedom. We have been working toward such a framework through a systematic quest for understanding of the complex semiclassical dynamics underlying the quantum spectrum of the molecule.

The main accomplishments achieved under this contract include: (1) determination of spectral patterns associated with phase space bifurcation structure and related spectral assignments with new quantum numbers; (2) assignment of spectra of polyatomics with three or more coupled degrees of freedom, following a bifurcation analysis of a chaotic Hamiltonian obtained from spectroscopic quantum fitting Hamiltonians; (3) the discovery of precessional modes in the bending spectra of acetylene, with assignment and related spectral patterns, following a bifurcation analysis of the spectral fitting Hamiltonian.

1. INTRODUCTION.

This report summarizes work on theoretical analysis of highly excited vibrational spectra of small molecules, continuing research conducted under AFOSR sponsorship under Contract F49620-92-J-0035. Significant strides have been made toward the ultimate goal of a comprehensive framework for systematic analysis of highly excited vibrational states of molecules. The basic motivation arises from the view that the traditional spectroscopic picture of states defined in terms of normal mode quantum number assignments is fundamentally inadequate for the highly excited, strongly coupled, anharmonic regime. All the work described here takes the general outlook that the road to progress lies in harnessing recent developments in nonlinear dynamical systems to problems of highly excited states. Detailed high-energy spectra of states with many quanta spread throughout the vibrational and rotation-vibration degrees of freedom present unprecedented challenges for spectral interpretation and organization of data into intelligible patterns. Traditional methods are predicated on assignment of eigenstates in terms of quantum numbers, such as the number of quanta in each normal mode, which are physically meaningful only in the low-energy, near-harmonic regime. In highly excited spectra, these zero-order quantum numbers are destroyed by the strongly coupled dynamics, which means the spectra become unassignable in ordinary terms. What is needed is a new or at least much more general framework for spectra complicated by strong interactions among some or all of the degrees of freedom. We have been working toward such a framework through a systematic quest for understanding of the complex semiclassical dynamics underlying the quantum spectrum of the molecule.

During the grant period, the PI visited the Phillips Laboratory at Hanscom Field in Massachusetts to explore technology transition opportunities with Dr. William Blumberg and co-workers concerned with highly excited small molecules. It is anticipated that this interaction will lead to fruitful exchange between the PI's academic research effort and issues of current technological interest to the Air Force. The overall aim is to devise new methods and physical concepts for organizing and interpreting large bodies of data on small molecules in environments with high degrees of excitation. Our work has progressed to the point where we can also seek specific data needed for our analyses of spectroscopic Hamiltonians.

Funds were used for partial support of three graduate students, Gengxin Chen, John Svitak, and Shuangbo Yang through June 15, 1992. Partial support was provided for two postdoctoral research associates, Dr. Zimin Lu and Dr. John Rose.

2. FIRST YEAR SUMMARY: November 1, 1991 - October 31, 1992.

Work progressed in two main directions. The first is a pattern recognition technique using correlation diagrams. The second, complementary direction is the use of bifurcation theory for multidimensional systems to analyze highly excited spectra. Where appropriate, principal references are given to earlier work, all of which was supported in part under earlier AFOSR Molecular Dynamics auspices (11/1/87 - 10/31/90).

A. Diabatic Correlation Diagram Pattern Recognition and Assignment

An early paper [1] proposed a "bootstrap" method for fitting spectra of chaotic systems which are unassignable in terms of usual normal modes quantum numbers. A second paper [2] described a "vector" method to deduce new quantum numbers from a multiple resonance fit of a spectrum. (This latter method is now being applied by R.W. Field and coworkers to stimulated emission pumping spectra of C₂H₂.) The bootstrap method of [1] is useful for fitting spectra of chaotic systems and obtaining potential surfaces [3]. However, it does not by itself yield quantum numbers for spectral pattern elucidation and assignment. The "vector" method of [2] does yield a partial set of quantum numbers. However, this set becomes smaller the higher the degree of chaos and the greater the detail of spectral resolution. A new development in our group, initiated in the first year of AFOSR sponsorship, combines the bootstrap fitting method, the "vector" assignment method, and a new phenomenological approach -- to be described shortly -- to obtain a complete set of quantum numbers. The new assignment approach is based on correlation diagrams. The assignment is made by taking account of diabatic energy level curves (near avoided crossings) in a correlation diagram from the zero-order to strongly coupled limits of the fit of an experimental spectrum. The fitting is strongly based on the "bootstrap" procedure. In this case, the bootstrap Hamiltonian uses effective resonance couplings, as opposed to potential surfaces used in other applications [3].

In the first funding year, we first tested this correlation diagram approach on relatively weakly coupled systems such as H₂O, using experimental energy levels, with apparently good results. We are now testing the correlation diagram method on model triatomic systems with a strong degree of chaos, using calculated energy levels, and appear to obtain meaningful results.

B. Bifurcation Analysis and Assignment of Multi-Dimensional Phase Space Structure

The second area is bifurcation theory analysis of phase space structure derived from experimental spectra. In earlier work [J. Chem. Phys. 93, 5805 (1990); 93, 5821 (1990) we showed how to give an exhaustive phase space classification of two-mode systems coupled by a strong Fermi resonance, resulting in a new dynamically based quantum number scheme. The goal is extension of this approach to the much harder problem of multidimensional systems. A primary goal is again to obtain new assignment schemes; a further object will then be to relate these to the spectral patterns and phenomenological assignments from the correlation diagram approach described above. It is expected that the bifurcation analysis will result in a much better understanding of the patterns we find with the correlation approach, which will probably be easier to implement in practice.

The status of the work in the first year was as follows. We have taken a standard spectroscopic fitting Hamiltonian for a triatomic with Darling-Dennison modes and Fermi resonance couplings. Taking the classical limit, we have established that the critical points of this Hamiltonian, which can be found analytically (i.e., without numerically solving Hamilton's equations), correspond to the period-1 orbits. This is very important because it is believed that in most cases, *the period-1 orbits determine most of the spectroscopically important structure of the molecular phase space*. The bifurcations of these period-1 orbits are analogous to the simple normal/local transition paradigm for stretches of a symmetric triatomic. Since we can solve this problem analytically for the spectroscopic Hamiltonian, the problem of assigning spectra of chaotic molecules will be largely simplified by this work.

Under separate sponsorship, we have been performing *analytical* analysis of standard fitting Hamiltonians for three-mode systems (triatomics), with successful results thus far. Under AFOSR sponsorship, Dr. John Rose, a postdoctoral research associate, has begun work on fitting and bifurcation analysis of four-atom systems, specifically, C₂H₂.

References for First-Year Summary:

1. J.M. Standard, E.D. Lynch, and M.E. Kellman, "Bootstrap Approach to Fitting Spectra of Molecules with Classically Chaotic Dynamics", J. Chem. Phys. 93, 159 (1990).
2. M.E. Kellman, "Approximate Constants of Motion for Vibrational Spectra of Many-Oscillator Systems with Multiple Anharmonic Resonances", J. Chem. Phys. 93, 6630 (1990).
3. J.M. Standard and M.E. Kellman, "Potential Energy Surfaces From Highly Excited Spectra Using the Bootstrap Method: Two-Dimensional Surfaces for Water and Ozone", J. Chem. Phys. 94, 4714 (1991).

4. L. Xiao and M.E. Kellman, "Catastrophe Map Classification of the Generalized Normal-Local Transition in Fermi Resonance Spectra", J. Chem. Phys. 93, 5805 (1990).
5. L. Xiao and M.E. Kellman, "New Assignment of Fermi Resonance Spectra", J. Chem. Phys. 93, 5821 (1990).

3. SECOND YEAR: November 1, 1992 - October 31, 1993.

We have been working in two main directions. The first is use of bifurcation analysis of the phase space of multidimensional systems to analyze highly excited spectra of coupled vibrational modes. The second, complementary direction is detection of patterns in highly excited spectra originating in bifurcations. A summary follows of the principal highlights of this work in the second year:

A. SPECTRAL PATTERNS AND MOLECULAR PHASE SPACE BIFURCATIONS

A major goal of our work is to uncover patterns in highly excited spectra which give signatures of phase space bifurcation structure. A manuscript in preparation in the second year [Ref. 14] accomplishes this for the first systems whose bifurcation structure we analyzed, the coupled stretches of a triatomic, and the Fermi resonance between a stretch and bend. Further manuscripts in preparation [Refs. 17, 18] explore these spectral patterns for novel torsional modes in acetylene and benzophenone.

B. FULL THREE-MODE BIFURCATION ANALYSIS AND ASSIGNMENT FOR H₂O

A major goal is methods to uncover the bifurcation structure of systems with many degrees of freedom, including chaotic dynamics. This has been accomplished, under separate support, for the stretches and bend of triatomics. Under AFOSR support, we worked in the second year toward using this bifurcation analysis to assign spectra of H₂O in highly excited chaotic states, using the correlation diagram technique described under First Year, Section A.

C. NOVEL PRECESSIONAL MODES IN ACETYLENE BENDS

A significant finding is the discovery of *precessional modes* in the spectrum of the coupled bending modes of benzophenone [Ref. 17 above]. This constitutes a new kind of correlated vibrational motion, related to normal modes, but representing a new kind of concerted motion of the vibrations.

Very unexpectedly, using parameters from an acetylene spectrum fit provided by the Field group at MIT, we have found precessional modes in the system of coupled acetylene bending modes [Ref. 18 above]. This may be especially significant in view of the expected importance of the bending modes in the acetylene-vinylidene isomerization problem.

4. THIRD YEAR: November 1, 1993 - October 31, 1994.

A. SPECTRAL PATTERNS AND MOLECULAR PHASE SPACE BIFURCATIONS

The procedure whereby vibrational spectra are classified by assigning normal mode quantum numbers to the vibrational states has proven immensely useful in molecular spectroscopy. Large numbers of levels are observed for which the normal mode assignments are well-defined and are very successful in organizing and interpreting the spectral data. In particular, progressions of normal mode overtone and combination levels have striking regularities in their intensities and energy level patterns which are immediately evident to visual inspection. However, it has become evident in recent years that the traditional expectation of assignability in terms of normal modes, with associated spectral regularity, is often fundamentally untenable for spectra in the highly excited regime. The combination of anharmonicity and strong coupling destroys the zero-order normal mode quantum numbers as dynamically meaningful assignments. With this breakdown of the usual assignment comes a more complex spectral pattern than the typical normal mode progressions. Indeed, in the regime of highly chaotic systems, it can be argued that there remains no residue whatsoever of spectral order interpretable in terms of the zero-order picture. But even in systems which are strongly coupled but not yet highly chaotic, the simple normal mode patterns break down. For example, at intermediate energies spectral phenomena occur such as the transition from normal to local modes, in which some levels are well-described in terms of normal modes, whereas others are better described in terms of local modes. In the special case of symmetric triatomics, one then sees the appearance of the conspicuous phenomenon of approximately degenerate "local mode doublets". Unfortunately, there is in general nothing so strikingly evident as local mode doublets to give an alternate means of organizing the data for the complex spectra of strongly coupled systems. The subject of this paper is an exploratory investigation of new kinds of spectral patterns for strongly coupled systems comparable -- in generality at least, if not quite in simplicity -- to those of the familiar patterns of normal mode systems. At this time, our investigations are confined to systems which are strongly coupled but not chaotic. Future work

will explore the more general problem of spectral patterns of chaotic systems. However, there is a very large body of important experimental work on non-chaotic systems to which the present investigation of spectral patterns has application.

Our goals are first to define prototype spectral patterns associated with abstract phase space structures, and then to evaluate the reliability of these patterns as markers of structure in the molecular phase space in analysis of experimental spectra. Our basic conclusions are the following. When the Hamiltonian used to fit a molecular spectrum indicates complicated phase space structure due to strong resonant coupling between anharmonic modes, this structure is evidenced by subtle but well-marked spectral patterns. Conversely, when such patterns occur in an experimental spectrum, then in order to reproduce these patterns in a reasonably behaved spectral fit, it is necessary and sufficient to invoke a resonant coupling term in the fitting Hamiltonian. The entire procedure is thereby internally consistent. Encoded in the spectral pattern is information as to whether the experiment has probed nontrivial phase space structure; this information is reliably decoded by means of the spectral fit.

This work resulted in a publication in the Journal of Chemical Physics (Ref. 14).

B. FULL THREE-MODE BIFURCATION ANALYSIS AND ASSIGNMENT FOR H₂O

In earlier work conducted partially under AFOSR auspices, we developed a method to extract dynamical information about molecules from analysis of fits of their spectra with spectroscopic fitting Hamiltonians. This has led to a systematic analysis using nonlinear dynamics tools such as bifurcation theory. The result was an essentially complete classification of the spectroscopic fitting Hamiltonian for two coupled modes. This has led to application of this analysis to assignment of spectral states in terms of new quantum numbers appropriate to the underlying dynamics. [L. Xiao and M.E. Kellman, J. Chem. Phys. 93, 5805 (1990); J. Chem. Phys. 93, 5821 (1990)].

Two further major steps are now needed for achievement of the desired complete framework for analyzing highly excited spectra. The first problem is phase space classification of systems with many degrees of freedom, and using this classification to assign the quantum spectrum. We are applying methods of bifurcation theory to this work. The second problem is detection of spectral patterns related to the resulting phase space classification and spectral assignment. I describe work on each of these problems in detail below.

Work prior to the current project focused on two modes coupled by a single resonance operator. A successful comprehensive approach to highly excited spectra has to confront directly the problem of many interacting degrees of freedom. This divides naturally into two parts. The first is identification of those dimensions of phase space actually affected by bifurcations. A very important by-product of this is identification of approximate constants of motion associated with the un-bifurcated degrees of freedom. These are associated with energy transfer pathways and "superpolyad" quantum numbers which are proving useful in other laboratories for accounting for some of the main features of complex spectra, in particular, fits of acetylene absorption spectra and hierarchies of splittings in dispersed fluorescence and SEP spectra. A solution to this problem has been presented with a theory [M.E. Kellman, J. Chem. Phys. 93, 6630 (1990); M.E. Kellman and G. Chen, J. Chem. Phys. 95, 8671 (1991)] of approximate constants of motion derived from spectral fitting Hamiltonians with multiple Fermi resonance couplings. The theory reduces to basic methods of vector algebra and leads to a simple "resonance vector" method which is quite easy to apply. The constants of motion correspond to "superpolyad" and other quantum numbers very useful for assigning complex spectra. We have been analyzing these quantum numbers in fits of experimental and simulated spectra of C₂H₂ currently being obtained in several laboratories. The resonance vector analysis has been applied by Field and coworkers at MIT to dispersed fluorescence and SEP spectra of acetylene in a model including vibrational angular momentum and vibrational *l*-resonance. They find that the superpolyad number is very useful for organizing information about energy transfer pathways, including the observation of hierarchies of feature and sub-feature structure corresponding to hierarchies of time scales for the energy flow.

The second part of the phase space analysis in higher dimensional systems is classification of the structure of the degrees of freedom which undergo bifurcations. The superpolyad quantum number permits a simplification similar to that in the two-mode system, in that it makes it possible to solve analytically for the large-scale bifurcation structure for spectroscopic fitting Hamiltonians of chaotic many-degree-of-freedom systems. This yields an exhaustive classification of the bifurcated phase space structure of the fitting Hamiltonian which leads to a set of quantum numbers appropriate to the classical dynamics underlying a given spectrum. The capability for the single resonance Hamiltonian of finding an analytical classification affords great insight into the molecular dynamics underlying the assignment. For chaotic systems, our expectation is that this classification will carry over to most physically important situations. This will happen if the *large-scale bifurcation structure* of the chaotic Hamiltonian is essentially that given by the single resonance approximate Hamiltonian. That this expectation is reasonable is indicated by our finding [J.M. Standard and M.E. Kellman, unpublished] that wave functions of

coupled stretches in ozone calculated on a potential surface are very similar to those of the single resonance fitting Hamiltonian. In particular, they exhibit with the same local/normal classification for spectral assignment.

It is desirable that the analysis of the many degree-of-freedom problem incorporate and generalize the above property of the single resonance Hamiltonian that it gives an analytic solution to the large-scale bifurcation structure and spectral assignment. At first this might appear unlikely, because the multidimensional Hamiltonian is likely to have more than one resonance, hence be chaotic. For example, a fit of the spectrum of all three vibrational modes of water requires not only a stretch-stretch coupling, but also a 2:1 Fermi resonance between the symmetric stretch and the bend. However, it is not the lack of chaos *per se* that allows an analytic classification for the single-resonance Hamiltonian. Rather, the key point is the existence of the conserved superpolyad number. The integrability of the single-resonance Hamiltonian that confines trajectories to invariant tori is merely a by-product of the superpolyad number. The crucial simplifying feature of the Hamiltonian for classifying phase space is therefore not that all the trajectories be integrable, but only that the large-scale bifurcation structure be analytically solvable. This analytic solvability as a consequence of the superpolyad number extends to many degree-of-freedom chaotic systems. The basic idea is that the large-scale bifurcation structure is defined by the lowest-order periodic orbits and their bifurcations. If the superpolyad number is a constant of motion, the lowest-order periodic orbits can be solved analytically, even for a multidimensional chaotic system.

This bifurcation analysis has been accomplished, and is now being applied to spectra of H₂O using the correlation diagram technique described under First Year, Section A.

C. NOVEL PRECESSIONAL MODES IN ACETYLENE BENDS

The goal of our work is new methods to analyze highly excited states of strongly coupled molecular vibrations. Recent work includes phase spheres, catastrophe map classifications, and new dynamically based quantum number assignments for benzophenone and acetylene. We believe a very significant finding in this work is the discovery of *precessional modes* in the spectrum of the coupled bending modes of acetylene. This constitutes a new kind of correlated vibrational motion, related to normal modes, but representing a new kind of concerted motion of the vibrations. Preliminary work under a previous AFOSR contract had suggested the presence of precessional modes in the benzophenone torsional system, and our current work confirms this.

Very unexpectedly, using parameters from an acetylene spectrum fit provided by the Field group at MIT, we have found precessional modes in the system of coupled acetylene bending modes. This may be especially significant in view of the expected importance of the bending modes in the acetylene-vinylidene isomerization problem. This work is being prepared for publication under Ref. 18.